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(54) **Ink jet printing method**

(57) An ink jet printing method, comprising the steps of:

- A) providing an ink jet printer that is responsive to digital data signals;
- B) loading the printer with ink-receptive elements comprising a support having thereon a porous ink-receptive layer;
- C) loading the printer with an ink jet ink composition

comprising a water-dispersible polymeric latex having contained therein a water-insoluble dye; and
D) printing on an ink-receptive substrate using the ink jet ink in response to the digital data signals.

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Description

[0001] This invention relates to an ink jet printing method which employs a porous receiver and an ink jet composition which provides improved light and dark stability.

[0002] Ink jet printing is a non-impact method for producing images by the deposition of ink droplets on a substrate (paper, transparent film, fabric, etc.) in response to digital signals. Ink jet printers have found broad applications across markets ranging from industrial labeling to short run printing to desktop document and pictorial imaging. The inks used in ink jet printers are generally classified as either dye-based or pigment-based.

[0003] A dye is a colorant which is molecularly dispersed or solvated by a carrier. The carrier can be a liquid or a solid at room temperature. A commonly used carrier is water or a mixture of water and organic co-solvents. Each individual dye molecule is surrounded by molecules of the carrier. In dye-based inks, no particles are observable under the microscope. Although there have been many recent advances in the art of dye-based ink jet inks, such inks still suffer from deficiencies such as low optical densities on plain paper and poor lightfastness. When water is used as the carrier, such inks also generally suffer from poor water fastness.

[0004] US-A-4,246,154 and US-A-5,852,074 relate to an ink jet ink composition comprising an water-insoluble dye dispersed in a water-dispersible polymer. However, there is a problem with this ink in that when it is printed onto a conventional receiver, the dry time is slow.

[0005] US-A-4,460,637 relates to a porous ink jet receiver element. However, there is a problem with this element in that when it is printed with a conventional aqueous dye-based ink, the printed image has poor light and dark stability.

[0006] It is an object of this invention to provide an ink jet printing method which provides an image which has a fast dry time. It is another object of this invention to provide an ink jet printing method which provides an image which has improved light and dark stability.

[0007] These and other objects are achieved in accordance with this invention which relates to an ink jet printing method, comprising the steps of:

- A) providing an ink jet printer that is responsive to digital data signals;
- B) loading the printer with ink-receptive elements comprising a support having thereon a porous ink-receptive layer;
- C) loading the printer with an ink jet ink composition comprising a water-dispersible polymeric latex having contained therein a water-insoluble dye; and
- D) printing on an ink-receptive substrate using the ink jet ink in response to the digital data signals.

[0008] The support for the ink-receptive element can be paper or resin-coated paper, or plastics such as a polyester-type resin such as poly(ethylene terephthalate), polycarbonate resins, polysulfone resins, methacrylic resins, cellophane, acetate plastics, cellulose diacetate, cellulose triacetate, vinyl chloride resins, poly(ethylene naphthalate), polyester diacetate, various glass materials, etc. The thickness of the support employed in the invention can be, for example, from 12 to 500 μm , preferably from 75 to 300 μm .

[0009] In a preferred embodiment of the invention the porous ink-receptive layer contains inorganic particles such as silica, alumina, titanium dioxide, clay, calcium carbonate, barium sulfate, or zinc oxide. In another preferred embodiment, the porous ink-receptive layer comprises from 20 % to 90 % inorganic particles and from 10 % to 80 % polymeric binder, such as gelatin, poly(vinyl alcohol), poly(vinyl pyrrolidone) or poly(vinyl acetate). The porous ink-receptive layer can also contain polymer micro-porous structures without inorganic filler particles as shown in US-A-5,374,475 and US-A-4,954,395.

[0010] A broad range of water-insoluble dyes may be used in the invention such as an oil dye, a disperse dye, a solvent dye, as disclosed in US-A-4,246,154 and US-A-5,852,074, or a metal-complex dye, such as the water-insoluble analogues of those described in US-A-5,997,622 and US-A-6,001,161, i.e., a transition metal complex of an 8-heterocyclyazo-5-hydroxyquinoline.

[0011] The dye-containing polymeric latex can be prepared by dissolving the dye in a water-miscible organic solvent, mixing the solution with the latex and then removing the solvent. Useful water-miscible organic solvents are water-miscible alcohols, ketones and amides, tetrahydrofuran, N-methyl-2-pyrrolidone, dimethylsulfoxide and mixtures thereof, such as acetone, ethyl alcohol, methyl alcohol, isopropyl alcohol, dimethylformamide, methyl-ethyl ketone etc.

[0012] The ink jet ink containing the water-dispersible polymeric latex employed in the invention consists of water as a continuous phase and dye-containing polymeric latex as a dispersed phase. In a preferred embodiment of the invention, the polymeric latex meets the following test: At 25° C., the polymeric latex must: (a) be capable of forming a stable dispersion with water at a concentration of from 0.2 to 50 percent by weight, preferably 1 to 20 percent by weight, and (b) when 100 ml of the latex is then mixed in an equal volume of the water-miscible organic solvent described above, stirred and allowed to stand for 10 minutes exhibit no observable coagulation of the polymeric latex. In order to be useful in the ink, the latex should have an average particle size of < 1 μm , preferably < 0.5 μm .

[0013] Aqueous lattices can be prepared by free radical polymerization or by condensation polymerization. Emulsion

polymerization is the preferred method of preparing polymer lattices. Monomers suitable to prepare the polymer lattices for this application include an acrylic acid, for example, acrylic acid, .alpha.-chloroacrylic acid, an .alpha.-alkylacrylic acid (such as methacrylic acid, etc.), etc., an ester or amide derived from an acrylic acid (for example, acrylamide, methacrylamide, n-butylacrylamide, t-butylacrylamide, diacetone acrylamide, methyl acrylate, ethyl acrylate, n-propyl acrylate, n-butyl acrylate, tert-butyl acrylate, isobutyl acrylate, 2-ethylhexyl acrylate, n-octyl acrylate, lauryl acrylate, tetrahydrofuryl acrylate, methyl methacrylate, ethyl methacrylate, n-butyl methacrylate, .beta.-hydroxy methacrylate, tetrahydrofuryl methacrylate, etc.), a vinyl ester (for example, vinyl acetate, vinyl propionate, vinyl laurate, etc.), acrylonitrile, methacrylonitrile, an aromatic vinyl compound (for example, styrene and a derivative thereof, vinyl toluene, divinyl benzene, vinyl acetophenone, sulfostyrene, etc.), itaconic acid, citraconic acid, crotonic acid, vinylidene chloride, a vinyl alkyl ether (for example, vinyl ethyl ether, etc.), an ester of maleic acid, N-vinyl-2-pyrrolidone, N-vinylpyridine, 2- or 4-vinylpyridine, etc. Of these monomers, an ester of acrylic acid, an ester of methacrylic acid, and styrene and styrene derivatives are particularly preferred. Two or more ethylenic unsaturated monomers can be used together. For example, a combination of methyl acrylate and butyl acrylate, ethyl acrylate and styrene, tetrahydrofuryl methacrylate and ethylacrylate, methyl acrylate and ethyl acrylate, etc., can be used.

[0014] The polymeric latex used in the invention can be prepared by emulsion polymerization or solution polymerization technique. Emulsion polymerization is preferred. Emulsion polymerization is well known in the art and is described, for example, in F. A. Bovey, Emulsion Polymerization, issued by Interscience Publishers Inc. New York, 1955. Examples of the chemical initiators which may be used include a thermally decomposable initiator, for example, a persulfate (such as ammonium persulfate, potassium persulfate, sodium persulfate), hydrogen peroxide, 4,4'-azobis (4-cyanovaleric acid), and redox initiators such as hydrogen peroxide-iron(II) salt, potassium persulfate-sodium hydrogensulfate, potassium persulfate-sodium metabisulfite, potassium persulfate-sodium hydrogen bisulfite, cerium salt-alcohol, etc. Emulsifiers which may be used in the emulsion polymerization include soap, a sulfonate (for example, sodium N-methyl-N-oleoylaurate, sodium dodecylbenzene sulfonate alpha-olefin sulfonate, diphenyloxide disulfonate, naphthalene sulfonate, sulfosuccinates and sulfosuccinamates, polyether sulfonate, alkyl polyether sulfonate, alkylaryl polyether sulfonate, etc.), a sulfate (for example, sodium dodecyl sulfate), a phosphate (for example, nonylphenol ethoxylate phosphate, linear alcohol alkoxylate phosphate, alkylphenol ethoxylate phosphate, phenol ethoxylate), a cationic compound (for example, cetyl trimethylammonium bromide, hexadecyl trimethylammonium bromide, etc.), an amphoteric compound and a high molecular weight protective colloid (for example, polyvinyl alcohol, polyacrylic acid, gelatin, etc.).

[0015] A second class of polymeric lattices used in the invention may be an aqueous dispersible polyester such as Eastman AQ® polyesters produced by the Eastman Chemical Company. The three polyesters, Eastman AQ 29, AQ 38, and AQ 55 are composed of varying amounts of isophthalic acid, sodium sulfoisophthalic acid, diethylene glycol, and 1,4-cyclohexanedimethanol. These thermoplastic, amorphous, ionic polyesters are prepared by a melt-phase condensation polymerization at high temperature and low pressure, and the molten product is extruded into small pellets. The solid polymer disperses readily in water at 70°C with minimal agitation to give translucent, low viscosity dispersions containing no added surfactants or solvents. Varying the amount of ionic monomers, i.e., sulfoisophthalic acid, can control the particle size. The particle sizes range from 20 to 100nm.

[0016] A third class of polymeric lattices used in the invention may be an aqueous dispersible polyurethane such as Witcobond® anionic and cationic polyurethane dispersion by Witco Corp. or Sancure® polyurethane by BF Goodrich Company.

[0017] A humectant is added to the composition employed in the process of the invention to help prevent the ink from drying out or crusting in the orifices of the ink jet printhead. Polyhydric alcohols useful in the composition of the invention for this purpose include, for example, ethylene glycol, diethylene glycol, triethylene glycol, propylene glycol, tetraethylene glycol, polyethylene glycol, glycerol, 2-methyl-2,4-pentanediol, 1,2,6-hexanetriol and thioglycol. As noted above, the humectant is employed in a concentration of from 10 to 50 % by weight. In a preferred embodiment, diethylene glycol or a mixture of glycerol and diethylene glycol is employed a concentration of between 10 and 20 wt. %.

[0018] A co-solvent can also be employed in the composition employed in the process of the invention. The selection of a co-solvent depends on the requirements of the specific application, such as desired surface tension and viscosity, the selected colorant, drying time of the ink jet ink, and the type of paper onto which the ink will be printed. Representative examples of watersoluble co-solvents that may be selected include (1) alcohols, such as methyl alcohol, ethyl alcohol, n-propyl alcohol, isopropyl alcohol, n-butyl alcohol, sec-butyl alcohol, t-butyl alcohol, iso-butyl alcohol, furfuryl alcohol, and tetrahydrofurfuryl alcohol; (2) ketones or ketoalcohols such as acetone, methyl ethyl ketone and diacetone alcohol; (3) esters, such as ethyl acetate, ethyl lactate, ethylene carbonate and propylene carbonate; and (4) sulfur-containing compounds such as dimethyl sulfoxide and tetramethylene sulfone.

[0019] The ink has physical properties compatible with a wide range of ejecting conditions, i.e., driving voltages and pulse widths for thermal ink jet printing devices, driving frequencies of the piezo element for either a drop-on-demand device or a continuous device, and the shape and size of the nozzle.

[0020] A penetrant (0-10 wt. %) may also be added to the ink composition employed in the process of the invention

to help the ink penetrate the receiving substrate, especially when the substrate is a highly sized paper. A preferred penetrant for the inks of the present invention is n-propanol at a final concentration of 1-6 wt. %.

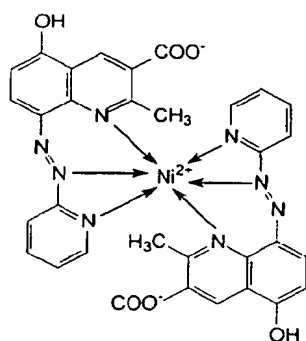
[0021] A biocide (0.01-1.0 wt. %) may also be added to prevent unwanted microbial growth which may occur in the ink over time. A preferred biocide for the inks of the present invention is Proxel® GXL (Zeneca Colours Co.) at a concentration of 0.05-0.5 wt. %. Additional additives which may optionally be present in ink jet inks include thickeners, conductivity enhancing agents, antikogation agents, drying agents, and defoamers.

[0022] Commercially available ink jet printers use several different methods to control the deposition of the ink droplets. Such methods are generally of two types: continuous stream and drop-on-demand.

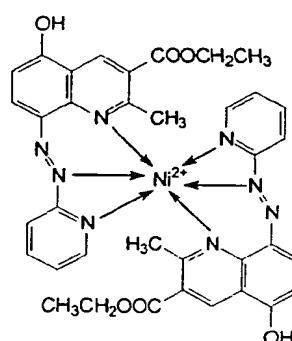
[0023] In drop-on-demand systems, a droplet of ink is ejected from an orifice directly to a position on the ink receptive layer by pressure created by, for example, a piezoelectric device, an acoustic device, or a thermal process controlled in accordance with digital data signals. An ink droplet is not generated and ejected through the orifices of the print head unless it is needed.

[0024] The following example illustrates the utility of the present invention.

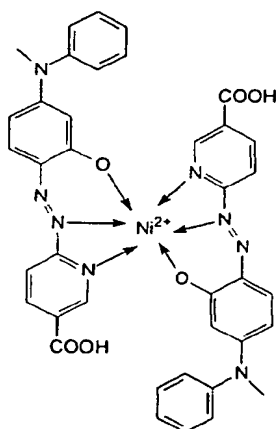
[0025] The following dyes were used in the Example:



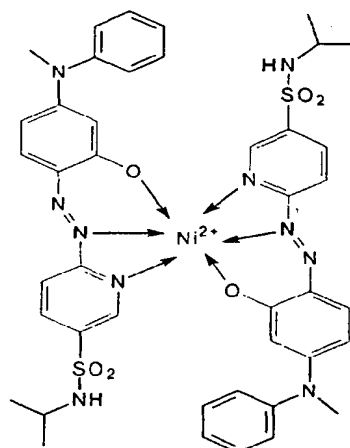
Water-soluble dye, Control Dye-1



Water-insoluble Dye 1
(Analogue of Control Dye-1)



Water-soluble dye, Control Dye-2



Water-insoluble Dye 2
(Analogue of Control Dye-2)

Comparative Element 1 (C-1)

[0026] To prepare comparative inkjet ink, 87 mg of Control Dye 1, 0.15g Surfynol® 465 (from Air Products), 0.75 g glycerol, 0.6 g diethylene glycol, 0.75 g propanol were added to 13.5 g distilled water. The ink pH was adjusted to approximately 8 by addition of triethanolamine or dilute sodium hydroxide. The final ink contained 0.58 % dye, and 1 % Surfynol® 465, 5 % glycerol, 4 % diethylene glycol and 5 % propanol. The solution was filtered through a 0.45 µm polytetrafluoroethylene filter and filled into a refillable inkjet cartridge.

[0027] A test image consisting of a series of 21 variable density patches, approximately 15 by 13 mm in size, ranging from 5% dot coverage to 100% dot coverage was printed onto commercially available Epson photo paper (Catalog NO. S041141), a porous receiver, with an Epson 200 inkjet printer. The sample was allowed to dry for 24 hours at ambient temperature and humidity.

Comparative Element 2 (C-2)

[0028] This element was prepared similar to Comparative Element 1 except that commercially available Konica QP Photo IJ Paper (Catalog No. KJP-LT-GH-15-QP PI), a porous receiver, was used instead of Epson photo paper. The results are also shown in Table 1.

Comparative Element 3 (C-3)

[0029] This element was prepared similar to Comparative Element 1 except that commercially available Mitsubishi Calcomp Glossy CJ paper (Catalog No. 8021601720), a porous receiver, was used instead of Epson photo paper. The results are also shown in Table 1.

Comparative Element 4 (C-4)

[0030] This element was prepared similar to Comparative Element 1 except that Control Dye 2 was used instead of Control Dye 1. The results are also shown in Table 1.

Comparative Element 5 (C-5)

[0031] This element was prepared similar to Comparative Element 2 except that Control Dye 2 was used instead of Control Dye 1. The results are also shown in Table 1.

Comparative Element 6 (C-6)

[0032] This element was prepared similar to Comparative Element 3 except that Control Dye 2 was used instead of Control Dye 1. The results are also shown in Table 1.

Element 1 of the Invention

[0033] An element similar to Comparative Element 1 was prepared except that AQ55 containing dye 1 was used instead of Control Dye 1. The AQ55 dispersion was prepared as follows: to 4.76 g of 31.5% commercially available dispersion AQ55 (from Eastman Chemical Co.) was added 10.2 g of water and 15.0 g of methanol. The resulting composition was stirred vigorously at room temperature to form the latex solution.

[0034] To prepare a dye solution, 150 mg of dye 1 was dissolved in a mixture of 6.0 ml of methanol and 6.0 ml of methylene chloride. The dye solution was then added dropwise to the above AQ55 dispersion with continuous stirring. After 1 hour, the organic solvent was removed under reduced pressure. The resulting stock solution was filtered through a 0.45 µm filter. The concentration of dye 1 in the latex stock solution was estimated to be 1%, and polymer concentration was ~10% by weight. To prepare the ink solution, 7.5 g of the above latex solution, 0.15g Surfynol® 465 (from Air Products), 0.75 g glycerol, 0.6 g diethyleneglycol, 0.75 g propanol were added to 5.25 g distilled water. No pH adjustment is necessary.

Element 2 of the Invention

[0035] An element similar to Element 1 was prepared except that commercially available Konica QP Photo IJ Paper (Catalog No. KJP-LT-GH-15-QP PI), porous receiver, was used instead of Epson photo paper. The dark and light fade results from the test images are shown in Table I.

Element 3 of the Invention

[0036] An element similar to Element 1 was prepared except that commercially available Mitsubishi Calcomp Glossy CJ paper (Catalog No. 8021601720), porous receiver, was used instead Epson photo paper. The dark and light fade results from the test images are shown in Table I.

Element 4 of the Invention

[0037] An element similar to Element 1 was prepared except that Dye 2 was used instead of Dye 1. The dark and light fade results from the test images are shown in Table I.

Element 5 of the Invention

[0038] An element similar to Element 4 was prepared except that commercially available Konica QP Photo IJ Paper (Catalog No. KJP-LT-GH-15-QP PI), a porous receiver, was used instead of Epson photo paper. The dark and light fade results from the test images are shown in Table 1.

Element 6 of the Invention

[0039] An element similar to Element 4 was prepared except that commercially available Mitsubishi Calcomp Glossy CJ paper (Catalog No. 8021601720), porous receiver, was used instead of Epson photo paper. The dark and light fade results from the test images are shown in Table I.

Stability Tests

[0040] The above step images were then subjected to light fade under 50 Klux high intensity daylight irradiation for a week and dark fade at 38 ° C, 80% relative humidity for a week. The Status A green reflection densities of maximum density patch of the said step images were measured using an X-Rite 820 @ densitometer before and after the fade test for light and dark, respectively. The % Retained in Status A green density for the 100% dot coverage patches were calculated and listed in Table 1.

Table I

Elements with Water-Soluble Dyes			Elements with Water-Insoluble Dyes		
Element	% Retained at Dmax		Element	% Retained at Dmax	
	Light	Dark		Light	Dark
C-1	83	96	1	93	104
C-2	12	27	2	97	88
C-3	80	68	3	97	99
C-4	40	80	4	84	91
C-5	63	79	5	80	90
C-6	69	81	6	86	88

[0041] The above results show that the elements of the invention had improved light and dark stability as compared to the control elements

Claims

1. An ink jet printing method, comprising the steps of:

- A) providing an ink jet printer that is responsive to digital data signals;
- B) loading said printer with ink-receptive elements comprising a support having thereon a porous ink-receptive layer;
- C) loading said printer with an ink jet ink composition comprising a water-dispersible polymeric latex having

contained therein a water-insoluble dye; and

D) printing on an ink-receptive substrate using said ink jet ink in response to said digital data signals.

2. The method of Claim 1 wherein said porous ink-receptive layer contains inorganic particles.

3. The method of Claim 2 wherein said inorganic particles comprise silica, alumina, titanium dioxide, clay, calcium carbonate, barium sulfate, or zinc oxide.

4. The method of Claim 1 wherein said porous ink-receptive layer comprises from 20% to 90 % inorganic particles and from 10 % to 80 % polymeric binder.

5. The method of Claim 4 wherein said polymeric binder is gelatin, poly(vinyl alcohol), poly(vinyl pyrrolidinone) or poly(vinyl acetate).

6. The method of Claim 1 wherein said water-dispersible polymeric latex comprises a polyester, a polyurethane or an acrylate.

7. The method of Claim 1 wherein said water-insoluble dye comprises an oil dye, a disperse dye, a solvent dye, or a metal-complex dye.

8. The method of Claim 7 wherein said metal-complex dye comprises a transition metal complex of an 8-heterocyclazo-5-hydroxyquinoline.



European Patent
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EUROPEAN SEARCH REPORT

Application Number
EP 01 20 0480

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
Y	US 5 707 722 A (IQBAL ET AL.) 13 January 1998 (1998-01-13) * column 6, line 4 - line 13 * * column 7, line 4 - column 8, line 2 * * column 8, line 66 - column 9, line 15 * * column 14, line 23 - line 34 *	1-8	B41M5/00 C09D11/00
Y	JP 55 018412 A (CANON) 8 February 1980 (1980-02-08) * page 4, left-hand column, line 17 - line 23 * * page 7, right-hand column, line 17 - line 32; claims 1,6 *	1-7	
D,Y	US 5 997 622 A (WEBER ET AL.) 7 December 1999 (1999-12-07) * column 1, line 13 - line 15; claims 1-4 *	8	
			TECHNICAL FIELDS SEARCHED (Int.Cl.7)
			B41M C09D
The present search report has been drawn up for all claims			
Place of search:		Date of completion of the search:	Examiner:
THE HAGUE		4 May 2001	Magrizos, S
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**ANNEX TO THE EUROPEAN SEARCH REPORT
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This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on
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04-05-2001

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5707722 A	13-01-1998	AU 7157396 A WO 9715455 A	15-05-1997 01-05-1997
JP 55018412 A	08-02-1980	JP 1453494 C JP 60032663 B	10-08-1988 29-07-1985
US 5997622 A	07-12-1999	EP 1006159 A JP 2000160078 A	07-06-2000 13-06-2000

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